No. 202408

Selective Extraction of Salts by Ditopic Receptors Bearing Various Coordination Sites

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Summary

Due to the lack of production of mineral resources in Japan, a stable supply is a particularly important issue. The recovery of such resources, including rare metals, from marine sources is a key focus, as is the recovery of mineral resources from urban waste. A wide variety of methods can be used to recover valuable metal salts from diverse resources; one of the most important of these is solvent extraction. Recently, we studied the extraction of various salts by solid-liquid extraction using flexible ditopic receptors with both cation and anion recognition sites. We found that receptor **1**, with ether linkers, can dissolve lithium chloride at high concentrations in organic solvents, such as acetonitrile. We also discovered that receptor **1** can selectively and efficiently extract lithium chloride from various salt mixtures, such as brine and bitterns, using a solid-liquid extraction system. Furthermore, we found that receptor **2**, with sulfur atoms instead of oxygen atoms, can extract softer salts, such as CuCl and AgCl, into organic solvents, such as chloroform. Transition metals are softer than alkali metals, but harder than soft metal cations, such as Cu(I) and Ag(I). In general, the order of softness of ligands is O < N < S. Replacing the coordination moieties with nitrogen atoms is expected to produce receptors with softness in the middle of receptors **1** and **2**. These receptors can be expected to strongly coordinate with the industrially important cations such as Mn(II), Co(II) and Ni(II), and to associate with counter anions via the anion recognition site, resulting in favorable ditopic receptors for transition metals, including rare metals. In this study, we designed receptors **3**–**5** that can coordinate with cations via aliphatic or aromatic amine moieties in the spacer and form multiple hydrogen bonds with urea moieties as anion recognition sites. We also designed receptors **6** and **7** that have heterocyclic nitrogens, such as quinoline or pyridine units, as cation recognition sites. We successfully synthesized these compounds via multi-step reactions. Furthermore, we qualitatively evaluated the solid–liquid extractability of several receptors and found that they are capable of extracting transition metal salts from a solid–liquid mixture as expected. We plan to evaluate the solid-liquid extractability of these synthesized receptors and the separation of valuable metals using multi-step extraction, including receptors **1** and **2**.